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CATHODO-LUMINESCENCE SPECTRA OF INDIAN FLUORITES

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Plates VIA and VIB

ABSTRACT. The cathodo-luminescence spectra of some chemically decomposed specimens of Indian fluorite in the visible and in the ultra violet region were studied using a direct-vision spectrograph and a Fuess quartz spectrograph For the examination of rare earths in fluorites, when they were converted into oxides, the luminescence exhibited was so bright that an exposure of 5–10 mins. was quite sufficient for taking a spectrogram. On inspection of the line-like bands in the luminescence spectra, it was ascertained that the activators for luminescence of decomposed specimens were Sm, Dy, Eu, Er, Nd, Gd and Tb. The rare-earths with even atomic number were the chief activators for luminescence with the exception of Eu of odd atomic number. For the strong activating ability of the above rare-earths, the presence of Pr could not, however, be ascertained definitely. In all specimens Sm acted as the chief activator for luminescence. It was concluded that, though Mn was present in all the specimens, the characteristic Mn-band in the visible region was suppressed in the luminescence spectra by the strong activating action of rare earths, when present in optimum quantity for strong activating ability The natural colour of fluorite was in no way connected with the varieties of rare-earths contained in it.

INTRODUCTION

The fluorides of rare-earths being highly insoluble the majority of natural fluorites contain rare-earth metals as minor constituents from below the range of detection to 0.1% – 0.2%. Such fluorites are in large numbers characteristically coloured and exhibit fluorescence or phosphorescence under the action of ultraviolet radiation, temperature elevation, cathode rays and X-rays.

Crookes (1883) observed by the action of cathode-rays on natural calcium compounds the appearance of citron yellow band in the luminescence spectra which he ascribed to yttrium; this was, however, proved by Urbain to be due to dysprosium. Urbain (1900) investigated on the cathodo-luminescence of coloured and uncoloured fluorites, particularly the specimen named as 'chlorophane,' remarkable for its green luminescence and found in the spectra the appearance of bands of Sm, Dy, Tb and Gd. The identification of observed bands was carried out referring to the spectra shown by the synthetical mixture of calcium fluoride and the pure rare-earths. The cathodo-luminescence spectra consisted of sharp line-like bands superimposed on broad diffuse bands; the wave-lengths of these lines of rare-earths were affected by the nature of base materials. Tanaka (1924) investigated on the cathodo-luminescence of 17 fluorites and found Sm as the chief active agent, other active agents being Y, Dy, Er, La, Ce and probably Yb. Wick (1924) found in 5 fluorites of England, in confirmation with Urbain's data, Sm, Dy, Gd and also Eu. According to Urbain La, Ce, Y and Yb, whose salts are colourless and devoid of absorption spectra, were found not to exhibit any such luminescence. Nichols and Howes (1926) studied various cases of the dominance and suppression of one activator

over another and concluded that the luminescence of Nd is suppressed by minute traces of either Sm or Pr and traces of Sm will suppress the luminescence due to traces of Pr, when the dilution is of the same order but that when Pr greatly preponderates, the Sm-bands are suppressed. They also observed that in a solution where Tb predominates the Dy bands disappear and in a solution in which Dy predominates both spectra appear. Yoshimura (1934) found in 10 Japanese fluorites chiefly Sm, Eu, Tb, Dy and in few Pr, Nd, Gd and Er as activators for cathodo-luminescence. These investigations showed that the presence of Sm, Eu, Tb, Dy, Nd, Pr, Er, that is, the coloured earths and also Gd is characterised by intense luminescence phenomenon by the action of cathode rays.

About the colouration of natural fluorites Yoshimura considered that the colour of fluorite was almost independent of the varieties of rare-earths contained in it and it was not possible to point out a special colour to be produced by the presence of certain definite element.

The object of the present investigation was to determine the rare-earths present in different specimens of Indian fluorite which were effective as activators for the luminescence and to trace the influence of other impurities present in fluorites on the luminescence spectra.

EXPERIMENTAL

The qualitative arc spectrographic analysis of the fluorites was carried out at 10 amps. 220 volts with a E_1 quartz spectrograph. The presence of rare-earths could not, however, be detected in any of the specimens. It was found that all the specimens of fluorite contained a measurable quantity of Mn. The method of cathodo-luminescence was then applied for the study of rare-earths in fluorites. The method of excitation for the specimens was by cathode rays obtained in a tube, designed according to Urbain (Fig. 1).

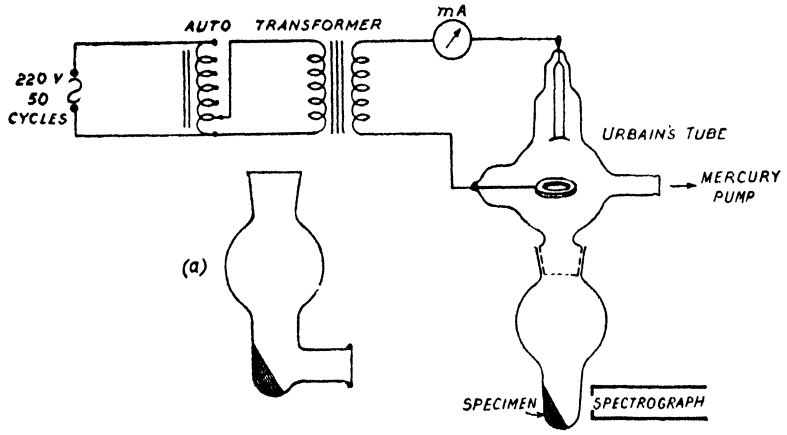


FIG. 1.

The vacuum in the cathode ray tube was maintained by one stage mercury pump run by a Cenco oil pump. A transformer with an auto-transformer was used as the source of excitation. The best condition for

excitation of the specimens was at 4000 volts. It was found necessary to keep the pump running continuously, otherwise the pressure in the tube increased slowly. This phenomenon was due to gases produced from the luminescent substance by the bombardment of the cathode rays. The intensity of luminescence was found to be maximum for all the specimens examined when the current in the tube was kept at 3.5 m A. The stop-cock connecting the tube with the mercury pump was constantly regulated in order to keep the current steady at 3.5 m A. The slight fluctuation in the current was found to be very effective for intense luminescence. The tube was cooled by an air-blower.

The intensity of luminescence exhibited by the fluorites was generally weak. In order to increase the luminescence chemical treatment of the fluorites was necessary. Urbain found that for the examination of rare-earths in fluorites when they were converted into sulphates the luminescence exhibited was more bright than when converted into oxides. In the present investigation it was found that the fluorites when converted into oxides the luminescence exhibited was so bright that an exposure of 5 mins. was quite sufficient for taking the spectrogram. Fluorite was powdered and then attacked with H_2SO_4 (analar) so as to remove HF and the excess H_2SO_4 was removed by slowly heating till no more fumes came out. The residual sulphate was dissolved by heating with 1 : 8 HCl (analar). Filtered and the filtrate was digested with liquor ammonia and $(NH_4)_2CO_3$ in excess so that they were all transformed into insoluble carbonate. The precipitate was washed free from SO_4^{--} with a dilute solution of $(NH_4)_2CO_3$ in dilute ammonia; then filtered, dried and ignited at nearly 800°C for 15 mins. in a muffle furnace. This oxide was exposed to cathode rays in the tube just after the heat treatment. The effect of the heat treatment at high temperature was that the intensity of the line-like bands was increased while that of the continuous background was decreased

For the study of the visible spectra, a direct-vision spectrograph was used. The spectrograph was fitted with an arrangement for photographing a graduated scale which served as a reference wave-length scale. The scale was calibrated with the lines of spectra of Li, He, Na, Ca, Tl, Sr, Cs, and iron arc spectrum. Before taking a spectrogram of the cathodo-luminescence spectrum, the mark 50 in the scale was always adjusted to coincide with the Na-line 5896 Å or 5890 Å. For the study of the ultraviolet spectra, the lower tube which contained the specimen was replaced by another, fitted with a quartz window at the side. The quartz plate was attached to a narrow prolongation of the sample holder with 'pecein' (Fig. 1.a). A Fuess quartz spectrograph was used and a Cu-arc spectrum was always taken along with the luminescence-spectrum of the specimen. The diaphragm had two slots, arranged as in Hartmann's diaphragm, of which the length of one was equal to the vertical height of the quartz window. After an exposure of the luminescence spectrum of the specimen, the slot of the diaphragm was

changed. The cathode tube was removed sideways and a quartz 90° prism was properly placed in front of the slit. The light of the Cu-arc was sharply focussed on the slit after passing through a quartz lens and the 90° prism.

The time of exposure for photographing the luminescence spectra in both spectrographs was 5-10 mins., panchromatic plates (31°) being used. The identification of the line-like bands in the spectra of different specimens, observed under a 'comparator' of nearly 10-times magnification, was carried out referring to Urbain's data for the different system of rare-earth oxide in calcium oxide (R_2O_3-CaO). As a preliminary work, synthetic mixtures of nearly 1.0% Sm, Pr and Gd oxides in CaO were prepared and their cathodo-luminescence spectra were photographed (time of exposure 5 mins.) which were almost identical with that of Urbain. The vacuum in the cathode ray tube being sufficiently high only a few faint lines of the discharge were recorded in the spectrum which were, however, eliminated from the tables. A standard mixture of 0.01% MnO_2 in CaO was prepared and its cathodo-luminescence spectrum was photographed. In order to get an idea of the relative intensities of different lines in the luminescence spectra of the specimens, photometric records of the spectrum plates were taken with a Moll Microphotometer. The wave-lengths of the Gd-lines in the ultra-violet spectrum were accurately measured with a 'comparator' of nearly 20-times magnification.

TABLE I

Rare-earths contained as activators in the chemically decomposed specimens of Indian fluorite

No. of specimen	Locality	Colour of specimen	Colour of cathodo-luminescence	Rare-earths contained as activators
*6251	Nandgaon and Khairagarh States, E.S.A.	Violet and green	Pink, blue tinge	Sm, Dy, Eu, Er (Tb)
*6688	Malhan, Jubbulpore, C. P.	Deep violet	Orange-yellow	Sm, Dy, Eu, Er, and Mn.
**1	Nandgaon, C.P.	,,	White, light orange-yellow tinge	,,
**2	,,	Green	Violet, yellow tinge	Sm, Dy, Eu, Er, Nd, Tb, Gd,
*3	Bastar State, Bhopalpatnam	Violet	White, yellow tinge	Sm, Dy, Eu, Er, Nd, Gd (Tb).
*4	Jaipur State, Rajputana	Green	Violet, orange tinge	Sm, Dy, Eu, Er, Nd, Tb, Gd,
*5	Chitral.	White, light green tinge	White, blue-violet tinge	Sm, Dy, Eu, Er, Nd, Gd (Tb).

* Specimen from Dr. A. K. Dey of Geological Survey of India.
** Specimen from Dr. H. K. Mitra of Tata Iron and Steel Co.

TABLE II

Wave-lengths of the line-like bands in the visible region observed in the luminescence spectra of chemically decomposed specimens. λ in I.Å

No. of Specimen						Rare-earths in CaO Urbain's data
6251	6688 & 1	2	3	4	5	
6663 m	*6603 m	6663 m	*6603 m	6663 m	*6603 m	6660 Sm
*6603 s	6474 f	*6603 s	6474 f	*6603 m	6474 f	6605 Sm
6474 m	6336 m	6474 f	6336 s	6474 f	6336 s	6470 Sm
6336 s	6261 s	6336 s	6261 ss	6336 s	6264 s	6310 Eu, 6330 Tb
6264 s	6243 s	6264 s	6243 ss	6264 s	6148 ss	6265 Sm
6243 s	6148 s	6243 m	6148 ss	6243 s	6051 ss	6245 Eu, 6240 Tb
6148 ss	6051 s	6148 ss	6051 ss	6148 ss	5931 m	6150 Sm, 6155 Eu
6120 f	5931 s	6051 ss	5931 s	6051 ss	5850 ss	6128 Eu
6051 ss	5850 s	5934 s	5850 s	5934 s	5763 ss	6052 Sm
5934 s	5826 s	5850 s	5826 s	5850 s	5684 ss	5930 Eu
5875 s	5763 s	5550 ss	5763 ss	5826 s	5558 m	5877 Dy, 5878 Tb
5850 s	5681 s	5826 s	5681 ss	5763 ss	5556 m	5848 Dy, 5843 Tb
5826 s	5505 f	5763 ss	5598 m	5684 ss	5406 m	5830 Dy
5763 ss	5556 f	5684 ss	5556 m	5658 m	5328 f	5760 Sm
5684 ss	*5182 f	5658 m	5492 m	5598 f	5184 f	5683 Sm
5658 m		5598 m	5406 f	5556 s	4938 m	5603 Er
5598 m		5556 m	5328 f	5526 m	4896 m	5501 Sm
5586 f		5526 m	5280 f	5492 m	4816 m	5550 Er, Tb
5556 s		*5184 f	5184 f	5406 m	4818 m	5527 Eu, 5521 Tb
5526 m		5406 s	5136 f	5398 f	4792 m	5495 Er, Tb
5192 f		5184 m	5061 f	5328 f	4766 f	5480 Sm
*5182 s		5136 m	5043 f	5280 f	4718 f	5505 Eu, 5400-5390 Tb
5106 f		4936 f	4936 f	5256 f	4726 ff	5330 Er
4896 m		4896 m	4816 m	5184 f	4690 f	5280 Er, Eu
4816 m		4796 s	4818 f	5136 f	4656 f	5225 Tb
4818 f		4846 m	4572 f	5061 m	4606 f	5180 Eu
4392 f		4818 m	4170 ff	5043 m	4572 f	5130 Eu
*4376 m		4792 s	4155 ff	5004 m	4512 ff	5063 Dy
4350 f		4766 m	4100 ff	4936 f	4470 ff	5015 Nd
4336 f		4718 m		4938 f	4155 ff	5000 Dy
		4690 m		4896 m		4935 Dy
		4656 f		4816 s		4910 Eu, 4900-4880 Dy
		4606 f		4818 s		4895 Tb
		4572 ff		4792 m		4815 Dy 4855 Tb
		4510 ff		4766 f		4815 Dy, 4805 Tb
		4512 ff		4718 f		4797 Dy
		4170 f		4690 m		4760 Er
		4155 f		4656 f		4755 Eu
		4100 f		4606 f		4718 Dy
		4392 f		4572 f		4705 Dy, 4720 Eu
		*4376 m		4512 f		4690 Nd, Er
		4350 m		4417 m		4685 Eu
		4335 m		4155 m		4660 Nd 4690 4665 Dy
				4100 m		4655 Eu
				*4392 f		4610 Nd
				*4376 m		4590 Er
				4335 m		4575 Nd
				4335 f		4550 Er
						4510 Dy
						4500 Er
						4515 Nd
						4490 Eu
						4470 Tb
						4460 Eu
						4460 Er
						4455 Tb
						4400 Nd, 4410 Tb
						4395 Tb
						4370 Tb
						4350 Tb
						4330 Eu

The intensities of the line like bands are expressed by the symbols, ss = very strong, s = strong, m = medium, f = faint ff = very faint

* These lines were coincident with faint lines of discharge

The calibration of the scale in the direct-vision spectrograph due to small dispersion

TABLE III

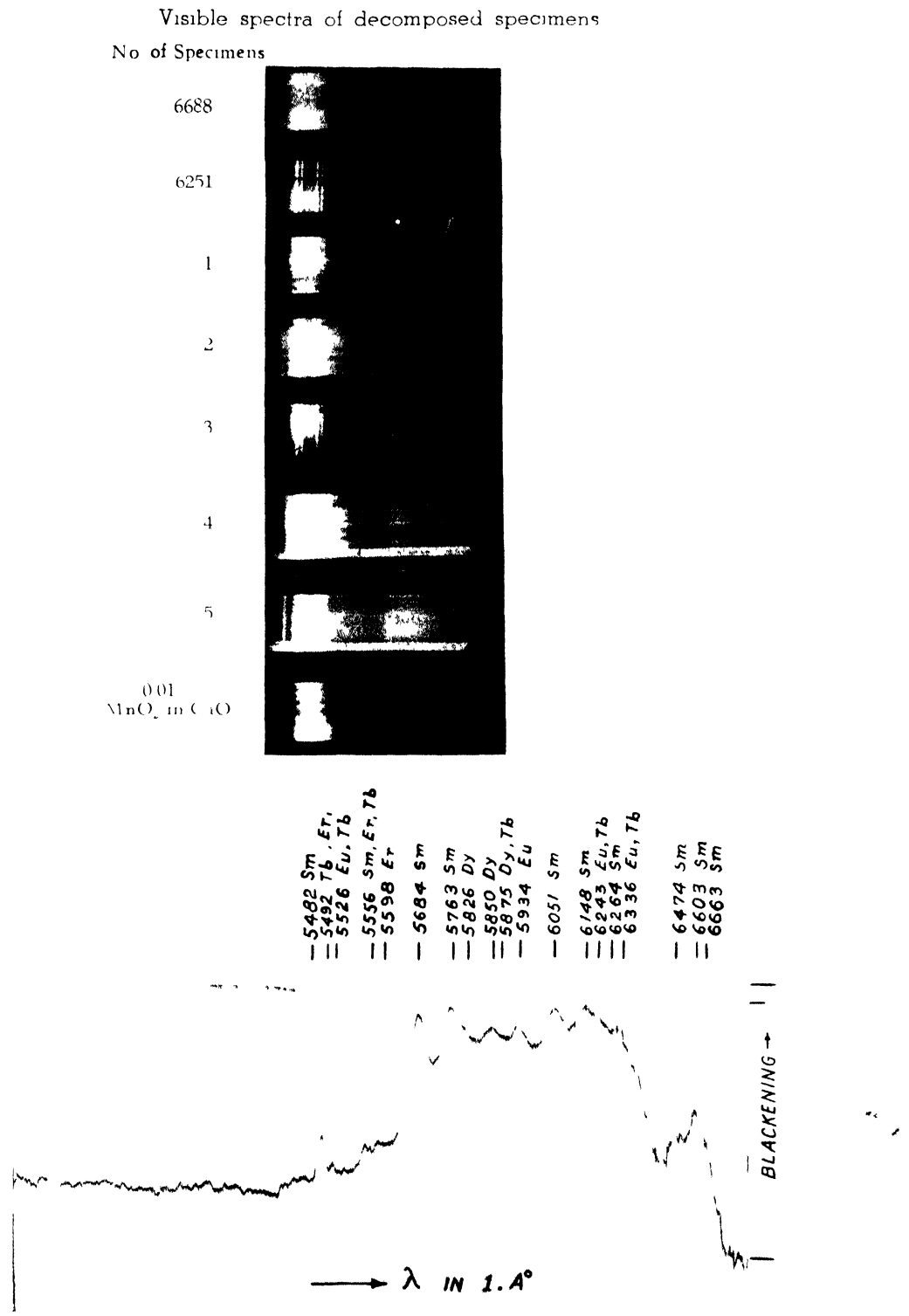
Wave-lengths of the line-like bands in the ultraviolet region observed in the luminescence spectra of chemically decomposed fluorites and corresponding maxima of gadolinium in calcium oxide. λ in I.A.

Specimen of fluorite				0.08% Gd_2O_3 in CaO	Urbain's data for (Gd_2O_3-CaO)
2	3	1	5		
3159 m	3159 s	3159 m	3159 m	3159 s 3155 s	3158 5 3155 5
3153 s	3153 ss	3153 s	3153 s	3153 ss	3153 0
3150 s	3150 m	3150 s	3150 s	3151 ss	3150 5
3146 s	3147 ss	3147 ss	3147 3143 } s	3147 ss	3147 0
3143 ss	3143 s	3143 s		3144 ss	3144 0
3140 f	3140 f	3140 f	3140 f	3140 ss	3140 5 3138 0
3135 m	3135 s	3135 f		3135 s	3136 0 3134 0
3130 m	3130 m			3130 m	3130 0
				3094 m	3091 0
				3088 f	3088 5
				3085 f	3085 0

INTERPRETATION OF RESULTS

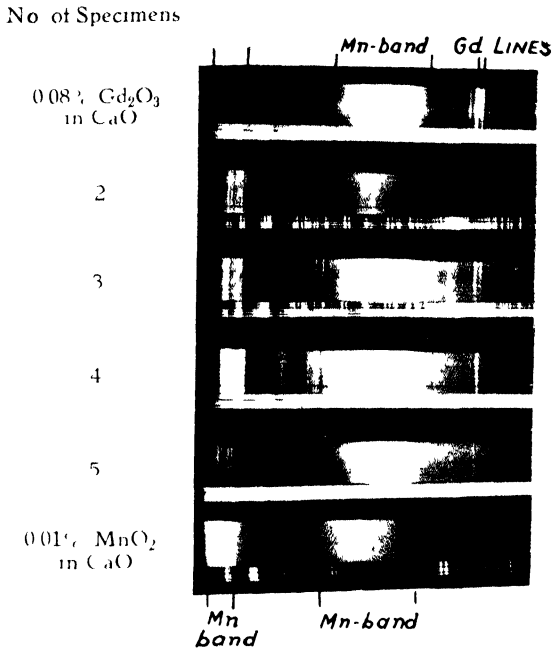
The cathodo-luminescence spectrum of 0.01% MnO_2 in CaO (orange-yellow luminescence) was found to be broad banded (from 6340 Å to 6150 Å and 6050 Å to 5560 Å) as to be practically continuous. All the specimens of fluorite contained traces of Mn. In specimen Nos. 1 and 6688 the line-like bands of rare-earths were superimposed on a strong background due to Mn which proved that the content of rare-earths in the two specimens not being the optimum quantity for strong activating ability, Mn also acted as an activator along with the rare-earths. The luminescence spectra of all other specimens consisted of strong line-like bands of rare-earths superimposed on very weak background. From this consideration, it may be concluded that when the rare-earths were present in optimum quantity for strong activating ability, the characteristic spectrum of Mn was totally suppressed leaving only the line-like bands produced by the activating action of different rare-earths.

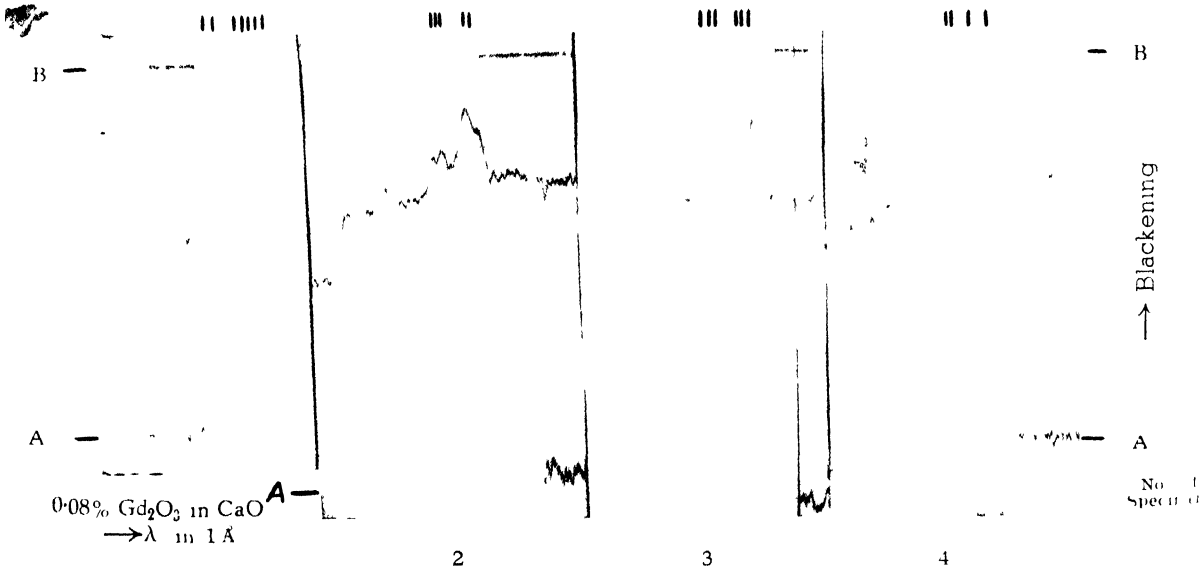
The calcium carbonate acting as a diluent contained traces of Mn and so exhibited, when converted to oxide, orange luminescence. Urbain (1911) found that there was no chemically pure calcium salt free from Mn and so



Photometric curve of Luminescence spectrum of chemically decomposed specimen No 6251

Ultra-violet spectra of decomposed specimens





Photometric Records of Gd - Lines

always exhibited bright orange to pale red luminescence according to the proportion under cathode rays. Urbain and Bruninghaus, however, after three months daily crystallisation obtained lime cathodically pure, that is, free from luminescence. In the present investigation the cathodo-luminescence spectra of all the specimens examined showed a continuous band in the ultraviolet region, from 4000 Å to 3400 Å approximately with maximum intensity in the region 3850 Å to 3500 Å. This characteristic strong band was also observed in the standard spectra of 0.08% Gd_2O_3 in CaO and of 0.01% MnO_2 in CaO. It is concluded that this characteristic band was not due to lime but due to the presence of Mn in the base material CaO and in the specimen. It was also found that while the characteristic Mn-band in the visible region was suppressed by the strong activating action of rare-earths, the characteristic band of Mn in the ultra-violet region appeared in the luminescence spectra of all specimens. From these facts, it is to be concluded that while Mn was present in all the specimens, the Mn-band was suppressed only in the visible spectra by the strong activating action of rare-earths, when present in optimum quantity.

The activators for luminescence in the specimens were Sm, Dy, Eu, Tb, Er, Nd and Gd. The characteristic line-like bands of Tb being faint, it is, probable that Tb (65) acted as a weak activator. It can be ascertained that rare-earths with even atomic number (Nd 60, Sm 62, Gd 64, Dy 66, Er 68) were the chief activators for luminescence with the exception of europium (Eu 63) of odd atomic number. The presence of Pr (59) of odd atomic number could not, however, be ascertained definitely because of the activating ability of the above rare-earths.

DISCUSSION

Yoshimura (*loc. cit.*) exposed natural fluorites to cathode rays and the time of exposure for taking a spectrogram was about 30-40 hours. Moreover, the cathode ray tube was frequently shaken in order to expose a fresh surface of the powdered sample as the intensity of luminescence was weak and decreased gradually by prolonged excitation of cathode rays. In the present investigation all the specimens of fluorite, when converted into oxides by chemical treatment, exhibited so bright a luminescence that an exposure of 5-10 minutes was quite sufficient for taking a spectrogram. Yoshimura (1934) also observed that green fluorites contained, in general, quite numerous rare-earths and the fluorites of the colours other than green contained a few of them. In the present investigation, the author found that the natural colour of fluorite was in no way connected with the varieties of rare-earths contained in it (Table I).

About the geochemical significance of the luminescence phenomenon, it was a point of much discussion whether Sm and Eu could be obtained primarily in the bivalent form or only in the presence of the reducing action of radioactive radiation. It was probable that the naturally fluorescing

fluorites were always radioactive or that radioactive radiations had influence on them. (Gmelins, 1938). Goldschmidt showed that tetravalent uranium and thorium could replace isomorphously the bivalent calcium in fluorspar. According to Goldschmidt, the fact that Eu was enriched in many minerals the same replacement might occur in the case of fluorspar. It was also long known that in certain minerals (*e.g.*, parisite, cordylite, yttrocerite and yttrofluorite) the fluorides of calcium, barium and the rare-earth elements were present in isomorphous mixture (Vogt, 1914). From all these facts, the author is rather inclined to believe that an isomorphous replacement of the bivalent form in question occurred in the case of fluorites.

In the previous note of the author (Mukherjee and Sarkar, 1947) the luminescence spectra of chemically decomposed specimens of fluorite was mentioned The associated white mineral in specimen No. 6688 examined was barite and in the cathodo-luminescence spectrum of this decomposed specimen only Mn (no rare-earths) acted as activator for luminescence.

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REFERENCES

Crookes, W., 1883, *Phil. Trans.*, **174**, 891.
Gmelins, 1938, *Handbuch der anorg. chemie.*, **39**, 15.
Mukherjee, B., and Sarkar, P. B., 1947, *Science and Culture*, **13** 209
Nichols, E. L., and Howes, H. L., 1926, *J. Opt. Soc. Am.* **13**, 573.
Tanaka, T., 1924, *J. Opt. Soc. Am.*, **8**, 501.
Urbain, G., 1909, *Ann. Chim. Phys* (8), **18**, 222.
1911, Spectrochimie, 169
Vogt, T., 1914, *Jahrb Min.*, **11**, 9.
Wick, F. G., 1924, *Phys. Rev.*, (2), **24**, 272.
Yoshimura, J., 1934 *Sc. Pap. I.P.C.R., Japan*), **23**, 224.